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Microwave dielectric properties and crystal structure of the tungstenbronze-type like $(Ba_{1-\alpha}Sr_{\alpha})_6(Nd_{1-\beta}Y_{\beta})_8Ti_{18}O_{54}$ solid solutions

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Abstract

A study of the dielectric properties, especially the $Q \times f$ value, of the tungstenbronze-type like $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solutions in $x = 0$ system was carried out. These compositions near $x = 0$ have very low $Q \times f$ values. To improve the $Q \times f$ value of these materials, we tried two substitutional systems, which are $(Ba_{1-\alpha}Sr_{\alpha})_6Nd_8Ti_{18}O_{54}$ and $Ba_4Sr_2(Nd_{1-\beta}Y_{\beta})_8Ti_{18}O_{54}$. In the former composition, the $Q \times f$ value was increased from 206 to 5880 GHz in the range of $0 \le \alpha \le 0.5$. And we found that Sr ions substituted for Ba ions in A1 sites have good effect on increasing the $Q \times f$ value, but Sr ions substituted for Ba ions in A2 sites have poor effect on increasing it. The latter composition also has a small effect on increasing the $Q \times f$ value.

Keywords: Composites; Dielectric properties; X-ray methods

1. Introduction

Many studies that describe the dielectric properties of the tungstenbronze-type materials have been reported. Ohsato et al.[1,2] studied the relation between the quality factor $Q \times f$ and their crystal structures in the $Ba_{6-3x}R_{8+2x}Ti_{18}O_{56}$ (R = rare earth) solid solutions (Table 1). They found that the $Q \times f$ value of those solid solutions have the maximum value at $x = 2/3$ because of a good ordering of Ba ions occupied all in large cations sites A2 and R ions occupied A1 sites. In the case of $x = 0$, A2 sites are occupied by four Ba ions, and A1 sites are occupied by two Ba ions and R ions. In this case, these materials have high internal strain and low $Q \times f$ value. Mercurio et al.[3] reported about the $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}La_{8+2x}Ti_{18}O_{54}$ solid solutions. They found that the maximum of the substitution was obtained for $x = 0$ and $\alpha = 0.33$, i.e., for $Ba_4Sr_2La_8Ti_{18}O_{54}$, and they also described that Sr ions occupied only the A1 (3) sites, which are conjunction sites of perovskite blocks denoted A1′ site by Mercurio et al. Ohsato et al.[4] also reported about the substitute of Sr for Ba in A1 sites.

In this study, we investigated to improve the $Q \times f$ value of the $Ba_6R_8Ti_{18}O_{54}$ solid solutions occupying all A1 and A2 sites. We will discuss the relation between dielectric properties and their crystal structures in this system. We tried two composition systems to improve the $Q \times f$ value of $Ba_6R_8Ti_{18}O_{54}$ solid solutions. The first composition is $(Ba_{1-\alpha}Sr_{\alpha})_6Nd_8Ti_{18}O_{54}$ $(0 \le \alpha \le 0.5)$, and the second composition is $Ba_4Sr_2(Nd_{1-\beta}Y_{\beta})_8Ti_{18}O_{54}$ $(0 \le \beta \le 0.5)$. Ba and Nd ions are substituted by Sr ions and Y ions, respectively, because Sr ions and Y ions have smaller ionic radii than Ba ions and Nd ions, respectively (Ba^{2+}, 1.47 Å; Sr^{2+}, 1.31 Å; Nd^{3+}, 1.109 Å; Y^{3+}, 1.019 Å by Shannon[5]).

2. Experiment

We prepared sintered ceramic pellets with 10 mm diameter and 5 mm thick using the conventional solid reaction method. The starting materials are $BaCO_3$, TiO_2, $SrCO_3$, Nd_2O_3 and Y_2O_3. Every material has purity over 99.9%. They were mixed in the ball mill and calcined at 1200–1300 °C for 2 h. The calcined and pulverized powders were pressed at 98 MPa into pellets and sintered at 1250–1350 °C for 2 h in air. Dielectric properties of the sintered ceramics were measured by Hakki–Coleman method using the network analyzer HP 8720B, and the accurate lattice parameters were obtained by using the Pawley method calculate by Rigaku JADE6.0 software.

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Table 1
Structural formula of the tungstenbronze-type crystal

Chemical formula		Structural formula	Q value
$Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$[1] R: rare earth	$x = 0$	$[R_8Ba_2]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$	High
	$x = 2/3$	$[R_{9.33}V_{0.66}]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$	Low
$(Ba_{1-\alpha}Sr_\alpha)_{6-3x}La_{8+2x}Ti_{18}O_{54}$[2]	$x = 0$ $\alpha = 1/3$	$[La_8Sr_2]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$	Unknown

3. Result and discussion

3.1. First system: $(Ba_{1-\alpha}Sr_\alpha)_6Nd_8Ti_{18}O_{54}$

The dielectric properties as a function of the composition α of $(Ba_{1-\alpha}Sr_\alpha)_6Nd_8Ti_{18}O_{54}$ are shown in Fig. 1. As shown in this figure, the $Q \times f$ value improved from 206 to 5880 GHz in the range of $0 \leq \alpha \leq 0.5$ as the amount of the substitution of Sr for Ba increased. In this range, the two critical points of α-values were recognized, which were $\alpha = 0.16$ and $\alpha = 0.26$. In the range of $0 \leq \alpha \leq 0.16$ the $Q \times f$ value increased gradually, but in the range of $0.16 \leq \alpha \leq 0.26$, the $Q \times f$ value increased steeply. Then the gradient is almost saturated in the range of $0.26 \leq \alpha \leq 0.5$.

The slope of the dielectric constant ε_r and the temperature coefficient of the resonance frequency τ_f also had the critical point at the same value $\alpha = 0.26$. ε_r decreased steeply from 122 to 103 in the range of $0 \leq \alpha \leq 0.26$, then decreased gradually in the range of $0.26 \leq \alpha \leq 0.5$ from 103 to 100. τ_f increased from −220 to +300 ppm/°C in the range of $0 \leq \alpha \leq 0.25$, but decreased from +300 to +169 ppm/°C in the range of $0.25 \leq \alpha \leq 0.5$. The reason of which all parameters have the same critical points will be discussed afterwards.

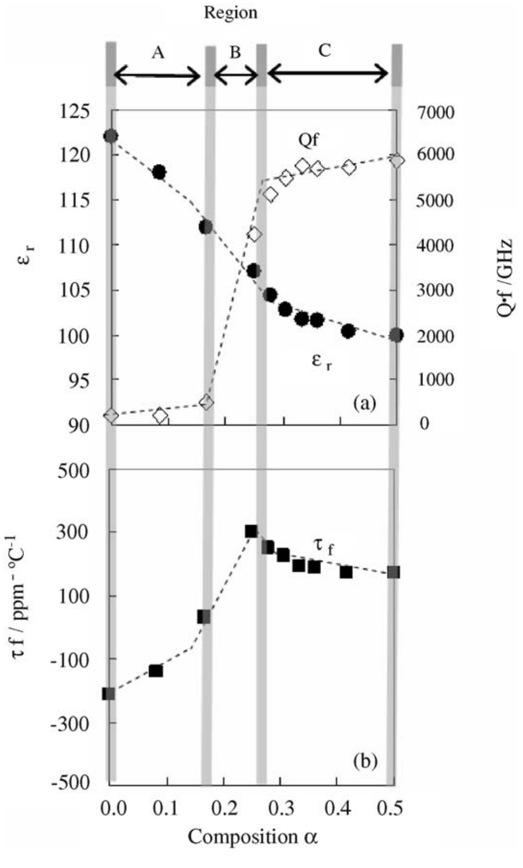

Fig. 1. (a) ε_r and $Q \times f$ vs. α; (b) τ_f vs. α in $(Ba_{1-\alpha}Sr_\alpha)_6Nd_8Ti_{18}O_{54}$.

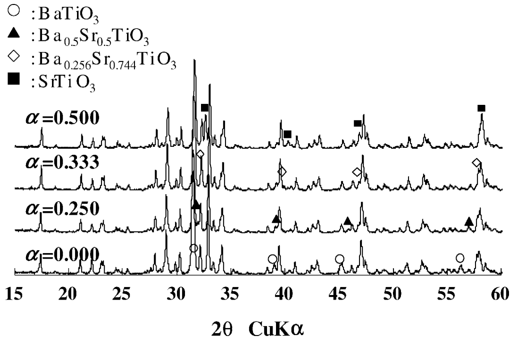

Fig. 2. XRD patterns of the $(Ba_{1-\alpha}Sr_\alpha)_6Nd_8Ti_{18}O_{54}$.

XRD patterns show that the tungstenbronze-type phase was recognized as a main phase in the whole range of our experiments as shown in Fig. 2. The change of the lattice parameters shows good linearity in the whole range as shown in Fig. 3. This linearity satisfies the Vegard's law and reflects the formation of the solid solution. The small secondary phases were also recognized in the whole range. They were identified as $BaTiO_3$ at $\alpha = 0$, and this phase shifted to $Ba_{1-x}Sr_xTiO_3$ as the Sr contents increased. Finally, it altered to SrTiO3 in the range of $0.4 \leq \alpha$.

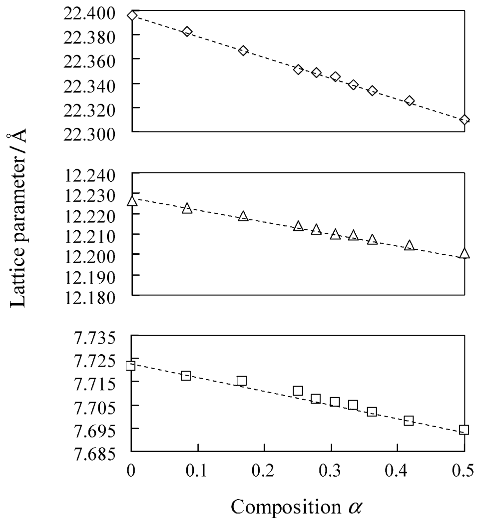

Fig. 3. The lattice parameters of the $(Ba_{1-\alpha}Sr_\alpha)_6Nd_8Ti_{18}O_{54}$.

Next is the discussion of the critical points. It becomes clear that two critical points divide the composition area into three regions: A, B and C as shown in Fig. 1. Ohsato et al.[6] presented that the limit of the $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{56}$ solid solutions was $x = 0.2$. This may be the reason of the formation of the secondary phase $Ba_{1-x}Sr_xTi_{18}O_{56}$ solid solutions in this study. So, this study's actual composition of the solid solutions might be $(Ba_{1-\alpha}Sr_\alpha)_{5.4}Nd_{8.4}Ti_{18}O_{54}$ $x = 0.2$, although the blended composition must be $x = 0$. On this assumption, all Ba ions in A1 sites are substituted by Sr ions at $\alpha = 0.26$. That is, at this composition, the chemical formula is $(Ba_{0.74}Sr_{0.26})_{5.4}Nd_{8.4}Ti_{18}O_{54}$, and the structural formula is $[Nd_{8.4}Sr_{1.4}V_{0.2}]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$.

So, in the region A and B, Sr ions substituted for Ba ions in A1 sites improved the $Q \times f$ value, because Sr ions, which have smaller ionic radii than Ba ions, decrease the internal strain of the $(Ba_{1-\alpha}Sr_\alpha)_6Nd_8Ti_{18}O_{54}$. In the region C, Sr ions substituted for Ba ions in A2 sites have poor effect in increasing the $Q \times f$ value. It is supposed that Sr ions do not decrease the internal strain enough, because the ionic radii of Sr ions are too small for large A2 sites. This is the reason of the critical point $\alpha = 0.26$.

In the region A, the presence of ferroelectric $BaTiO_3$ secondary phase, which has a large dielectric loss, might disturb the steep increase of the $Q \times f$ value. And in the regions B and C, the secondary phases shift to dielectric materials, i.e., $Sr_{1-x}Ba_xTiO_3$ and $SrTiO_3$, which have smaller dielectric loss than ferroelectric. So, the $Q \times f$ value may not be disturbed in the regions B and C.

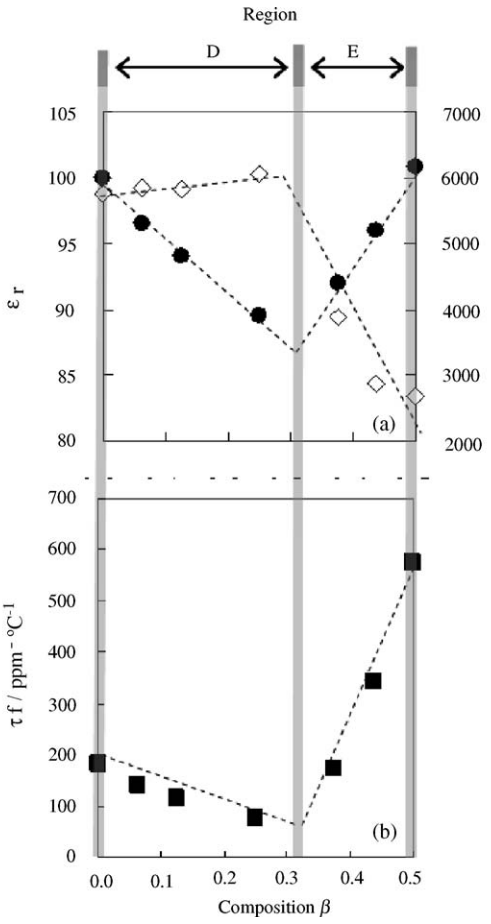

Fig. 4. (a) ε_r and $Q \times f$ vs. β (b) τ_f vs. β in $Ba_4Sr_2(Nd_{1-\beta}Y_8)Ti_{18}O_{54}$.

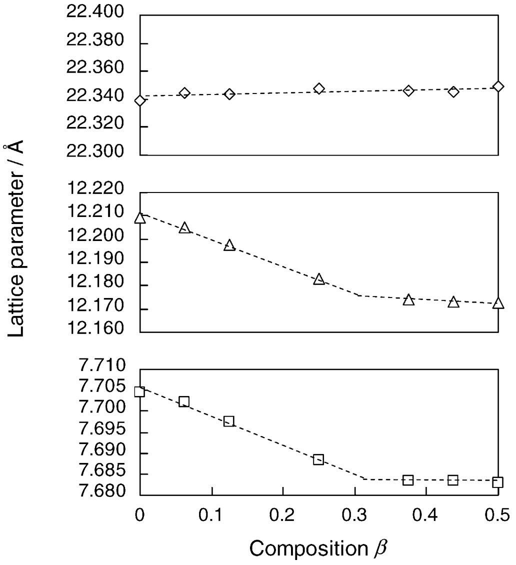

Fig. 5. The lattice parameters of the $Ba_4Sr_2(Nd_{1-\beta}Y_8)Ti_{18}O_{54}$.

3.2. Second system: $Ba_4Sr_2(Nd_{1-\beta}Y_\beta)_8Ti_{18}O_{54}$

The dielectric properties as a function of the composition β are shown in Fig. 4. As shown in this figure, the β value has a critical point at $\beta \approx 0.3$. This critical point divides these compositions into two regions, D and E. The slope of the lattice parameters shown in Fig. 5 say that the limit of the $Ba_4Sr_2(Nd_{1-\beta}Y_\beta)_8Ti_{18}O_{54}$ solid solutions is $\beta = 0.32$. This value must be the critical point of these compositions. In the region D, the substitution for Nd ions by Y ions improved the $Q \times f$ value, and decreased ε_r and τ_f. In the region E, the secondary phases $Y_2Ti_2O_7$ and $Ba_4Ti_{13}O_{30}$ shown in Fig. 6 deteriorated the $Q \times f$ value increase. Additionally, ε_r and τ_f were increased in this region.

The second system is summarized that the substitution for Nd ion by Y ion has a weak effect on improvement the $Q \times f$ value in the range of $0 \leq \beta \leq 0.32$, because the difference of the ionic radii between Nd and Y is not large, i.e., 0.09 Å, and the limit of the solid solution of $Ba_4Sr_2(Nd_{1-\beta}Y_\beta)_8Ti_{18}O_{54}$ is $\beta = 0.32$.

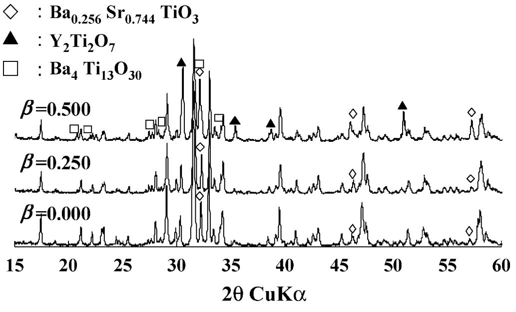

Fig. 6. The XRD patterns of the $Ba_4Sr_2(Nd_{1-\beta}Y_8)Ti_{18}O_{54}$.

4. Conclusions

We studied how to improve the $Q \times f$ value of the tungstenbronze-type like $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}(Nd_{1-\beta}Y_{\beta})_{8+2x}Ti_{18}O_{54}$ solid solutions in $x = 0$ system. For this purpose, we tried two systems. First system is $(Ba_{1-\alpha}Sr_{\alpha})_6Nd_8Ti_{18}O_{54}$ and the second system is $Ba_4Sr_2(Nd_{1-\beta}Y_{\beta})_8Ti_{18}O_{54}$.

In the first system, we found that Sr ions substituted for Ba ions improved the $Q \times f$ value from 206 to 5880 GHz in the range of $0 \leq \alpha \leq 0.5$. And in this range, the α value has two critical points $\alpha = 0.16$ and $\alpha = 0.26$, which divide the composition into three regions, A, B and C. In the regions A and B, Sr ions substitute for Ba ions in A1 sites, which have good effect on improvement the $Q \times f$ value originally. But in the region A, the $Q \times f$ value increase gradually. In this region, the presence of ferroelectric $BaTiO_3$ secondary phase might disturb the steep increase of the $Q \times f$ value. In the region C, Sr ions substituted for Ba ions in A2 sites have the weak effect on improvement the $Q \times f$ value.

In the second system, Y ions substituted for Nd ions also have a slight effect on improvement of the $Q \times f$ value in the range of $0 \leq \beta \leq 0.32$, and the limit of the solid solution of $Ba_4Sr_2(Nd_{1-\beta}Y_{\beta})_8Ti_{18}O_{54}$ is $\beta = 0.32$.

References

1. Ohsato, H., Science of the tungstenbronze-type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) microwave dielectric solid solutions. *J. Eur. Ceram. Soc.*, 2001, **21**, 2703–2711.
2. Ohsato, H., Imaeda, M., Takagi, Y., Komura, A. and Okuda, T., Microwave quality factor improved by ordering of Ba and rare-earth on the tungstenbronze-type $Ba_{6-3x}R_8+2_xTi_{18}O_{54}$ (R = La, Nd and Sm) solid solutions. In *Proceeding of the XIth IEEE International Symposium on Applications of Ferroelectrics*. IEEE catalog number 98CH36245, 1998, pp. 509–512.
3. Mercurio, D., Abou-Salama, M. and Mercurio, J.-P., Investigations of the "tungsten-bronze"-type $(Ba_{1-\alpha}Sr_{\alpha})_{6-x}(La_{8+2x/3}Ti_{18}O_{54}(0 \leq x3)$ solid solutions. *J. Eur. Ceram. Soc.*, 2001, **21**, 2713–2716.
4. Imaeda, M., Mizuta, M., Ito, K., Ohsato, H., Nishigaki, S. and Okuda, T., Microwave dielectric properties of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions substituted Sr for Ba. *Jpn. J. Appl. Phys.*, 1997, **36**(9B), 6012–6015.
5. Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, 1976, **A32**, 751–767.
6. Ohsato, H., Ohhashi, T., Nishigaki, S., Okuda, T., Sumiya, K. and Suzuki, S., Formation of solid solutions of new tungsten bronze-type microwave dielectric compounds $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$. *Jpn. J. Appl. Phys.*, 1993, **32**, 4323–4326.